

PRODUCTION OF CETANE IMPROVER FROM *Jathropa curcas* OILAbdullah^{1*}, Wicakso, D.R.², Junaldi, A.B.¹, and Badruzsaufari³¹Department of Chemistry, Lambung Mangkurat University, Jl. A. Yani Km 36 Banjarbaru, South of Kalimantan²Department of Technical Chemistry, Lambung Mangkurat University, Jl. A. Yani Km 35.8 Banjarbaru. South of Kalimantan³Department of Biology, Lambung Mangkurat University, Jl. A. Yani Km 35.8 Banjarbaru. South of Kalimantan

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ABSTRACT

Nitration of biodiesel from *Jatropha curcas* oil using mixture of HNO_3 and H_2SO_4 had been done in an attempt to obtain a cetane improver or cetane number enhancer. The nitration was carried out by varying the numbers of moles of sulphuric acid, nitric acid, temperature and time. The process was conducted in a round bottom flask reactor that equipped with a magnetic stirrer and a ball cooler on a water bath. The mixture of H_2SO_4 and HNO_3 was placed in the reactor and subsequently added slowly with biodiesel drop by drop. The results showed that increasing the mole numbers of sulphuric acid tends to reduce the yield or volume and total N of nitrated biodiesel. Increasing the number of moles of nitric acid tends to increase the yield, but decrease the value of total N. While increasing of temperature and reaction time tends to reduce the yield and total N. From FTIR spectra product was estimated as a mixture of esters of alkyl nitrates and nitro. From the testing of cetane number it can be predicted that nitrated biodiesel potentially as cetane improver.

Keywords: cetane improver, jatropha oil, additive, diesel oil

INTRODUCTION

Cetane improver is an additive that improves the cetane number of diesel fuel. Addition of cetane improver in fuel may make exhaust gas more friendly to environmental with decrease carbon monoxide and oxide of nitrogen [1]. Cetane improver can be produced by reacting biodiesel with nitric acid in nitration process [2-4], while biodiesel can be produced from *Jatropha curcas* oil through esterification and transesterification [5-8]. Nitration process can enhance the number of oxygen atoms in the molecules of biodiesel components can be increased. Addition of oxygen atoms to those components is in the form of NO_2 or NO_3 [9]. Thus, biodiesel become rich in oxygen atoms that are used for the completion of the combustion process [10]

Nasikin et al. [3] has succeeded to produce nitrated biodiesel from coconut oil in mixture of HNO_3 and H_2SO_4 . Addition of 1.5% (v/v) of cetane improver may increase diesel cetane number from 44.68 to 48.21, which is equivalent to the value of the cetane number of mix of 80% diesel oil with 20% biodiesel (B20). While Rabello et al. [11] reported that castor oil nitration using a blend 72% (w/w) acetic anhydride and HNO_3 as much as 28% (w/w) of the oil at 15 °C produced good cetane improver. The supplement of the nitration products as much as 1000 mg/L can increase the cetane number of diesel oil as much as 3 units.

In the nitration process of biodiesel, NO_3 or NO_2 will attached to the double bonds of carbon atom. Thus,

the more double bonds in biodiesel molecules the higher the probability of nitration occurs. Base on the previous argument, biodiesel which was derived from *Jatropha* oil has a great potential material in the production of cetane improver. In addition, the availability of *Jatropha* is relatively abundant and does not compete with food needs.

EXPERIMENTAL SECTION

Materials

Jatropha curcas oil (BALITTAS, Malang), methanol (CH_3OH), sulphuric acid (H_2SO_4), nitric acid (HNO_3), potassium hydroxide (KOH), phosphoric acid (H_3PO_4), isopropyl alcohol, Wijs solution, potassium iodide (KI), carbon tetrachloride (CCl_4), starch, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sodium thiosulfate, copper sulfate hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sodium sulfate, sodium hydroxide (NaOH), hydrochloric acid (HCl). All chemicals are pro analysis (p.a) grade of E. Merck, universal pH paper (E. Merck), aquadest (Laboratory of Faculty of MIPA, University of Lambung Mangkurat)

Instrumentation

Glass apparatus used include Beaker glass, Erlenmeyer flask, separating funnel, volumetric flask, volumetric glass, pipette drops, pipette volume. Other equipments used were a set of reflux apparatus, a set

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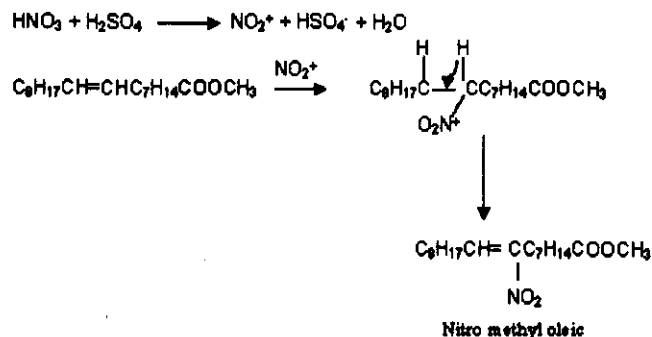


Fig 3. Nitro compound formations through the nitration of methyl oleate

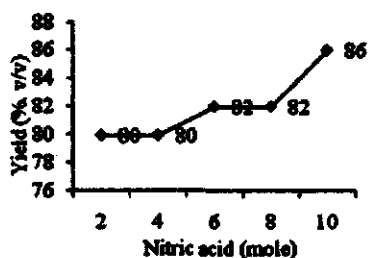


Fig 4.a The relationship between numbers of moles nitric acid to yield

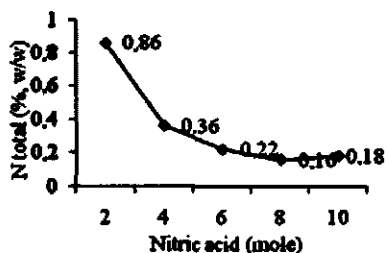


Fig 4.b The relationship between numbers of moles nitric acid to N total

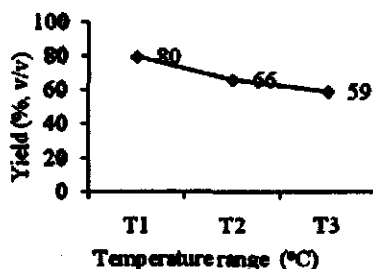


Fig 5.a Graph showing the relationship between temperature ranges to yield

Effect of Temperature Changes and Reaction Time on Biodiesel Nitration

Nitration of biodiesel was also carried out in different range of reaction temperature. Alteration of

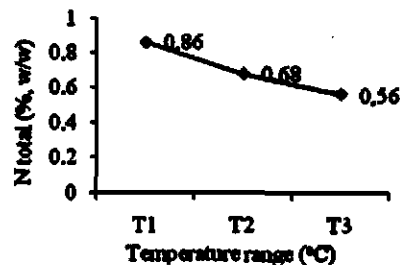


Fig 5.b Graph showing the relationship between temperature ranges to N total

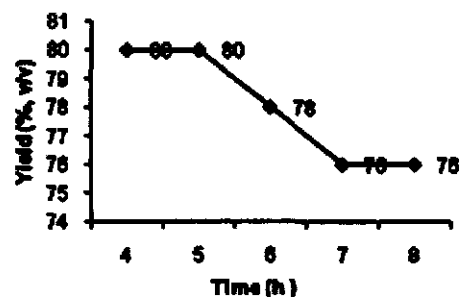


Fig 6.a The relationship between reaction time to yield

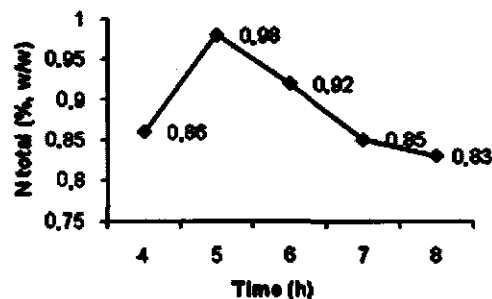


Fig 6.b The relationship reaction time to N total

temperature was expected to enhance the reaction performance. High temperatures will cause an increase in kinetic energy of molecules, so that the intensity of collisions between reactants molecule become higher. Thus the activation energy of the reaction can be easily exceeded. In this research the reaction was performed in gradual increase of temperature range starting at 10-20 °C (T₁), and then at 20-30 °C (T₂) and lastly at 30-40 °C (T₃).

Fig. 5.a and Fig. 5.b shows that increasing temperature resulted in the decreasing yield and total N of nitrated biodiesel. The decrease was predicted as a result of the reduction of nitration product which may be dissolved in hexane during extraction process. Nitration reaction was also performed by varying the reaction time in order to find the optimum time of this nitration. The

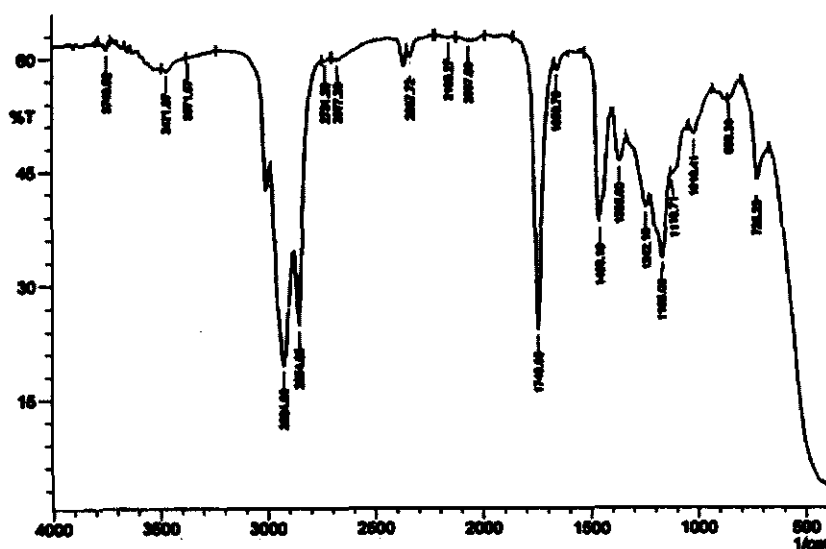


Fig 7.a IR spectra of biodiesel

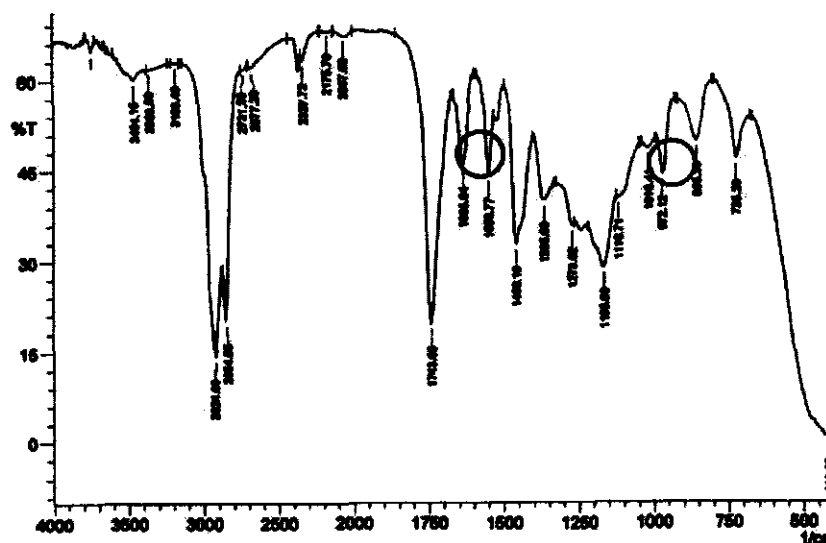


Fig 7.b IR spectra of nitration product

optimum time in the nitration of biodiesel is 5 h (Fig. 6.a and Fig. 6.b).

Biodiesel and Nitration Products Analysis Using Spectrometer FTIR

Characterization of biodiesel and nitration product was conducted by Infra Red (IR) spectrometer to determine the existence of new functional groups on the results of nitration products. Fig. 7.a and Fig. 7.b show that there were new spectrums that appear at wave numbers 1635.64, 1550.77 and 972.12 (cm^{-1}) that

indicated the absorption spectrum of $-\text{NO}_3$ or $-\text{NO}_2$ which attached to the molecules of biodiesel.

The spectrum at wave numbers 1635.64 cm^{-1} was supposed to be derived from nitrate groups. The spectrum at wave numbers 1550.77 cm^{-1} was presumed to be derived from the vibration of the bond between N atom of $-\text{NO}_2$ with O atom, while the spectrum at wave numbers 972.12 cm^{-1} originating from the $-\text{CN}$ bond stretching [3], where N atom derived from $-\text{NO}_2$ and C atom derived from biodiesel. Based on these data, it can be assumed that the molecule of biodiesel which was produced in the form of alkyl nitrate ester and nitro alkyl esters.

Table 1. Flash point and cetane number of nitration product

Parameter	Unit	Sample			Method
		NME 0.1	NME 0.5	Diesel Oil	
Flash Point	°C	69	69	69	ASTM D 93
Cetane number	-	47.1	48.8	46.3	ASTM D 613

NME : Nitrated Methyl Ester

NME 0.1 : Mixture of NME 0.1% + Diesel oil 99.9%

NME 0.5 : Mixture of NME 0.5% + Diesel oil 99.5%

Analysis of Iodine Number of Biodiesel and Nitration Product

The results showed that the nitration process in biodiesel has changed the value of iodine number. Numbers of iodine (g I₂/100 g) for the methyl ester is 267 and after the nitration decreased to 150. This decrease was caused by a reduced number of double bonds in the molecule of biodiesel. This could strengthen the reason that the nitration process has occurred.

Effect of Nitration Products on the Flash Point and Cetane Number of Diesel Oil

Nitration products were also measured flash point value and the cetane number. The measurement results for each sample is as indicated in Table 1.

Based on the data of the above table, it can be deduce that the cetane improver which was produced did not affect the value of flash point. While based on the cetane number value, addition of nitrated product of 0.1% (NME 0.1) and 0.5% (NME 0.5) to diesel fuel could increase the cetane number value 0.4 and 2.5 units respectively.

CONCLUSION

Increasing the number of moles of sulphuric acid tends to decrease the yield and total N of nitrated products. Increasing the number of moles of nitric acid tends to increase yield, but the value of total N decreased. Increasing temperature and reaction time tends to reduce yield and total N of nitration products. Nitration products from this nitration were assumed as alkyl ester compounds or nitro alkyl nitrate ester. Based on the cetane number, the nitrated biodiesel from this research potentially acts as a cetane improver.

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